

Sulfurization of polymers

1. The reaction of polydialkylsiloxanes with elemental sulfur and electrochemical behavior of the products

B. A. Trofimov,^a T. A. Skotheim,^b L. V. Andriyankova,^{a*} A. G. Malkina,^a G. F. Myachina,^a
S. A. Korzhova,^a T. I. Vakul'skaya,^a I. P. Kovalev,^b and Yu. V. Mikhailik^b

^aIrkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences,
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.

Fax: +7 (395 2) 35 6046. E-mail: bat@acet.irkutsk.su

^bMoltech Corporation,

9062 South Rita Road, Building 61, Tucson, Arizona, USA.

Fax: (520) 799 7501

Polydiethylsiloxane reacts with elemental sulfur at 300–320 °C (ZnCl₂ slightly accelerates the process) with evolution of hydrogen sulfide and formation of black lustrous paramagnetic powders (sulfur content up to 38.50%), which possess a noticeable electric conductivity ($3.20 \cdot 10^{-7}$ S cm⁻¹ when doped with I₂) and redox properties. Polydimethylsiloxanes are stable under the same conditions. In rechargeable lithium batteries, the sulfurized polydiethylsiloxane behaves as an active cathode material allowing charging and discharging of the battery. The specific capacities of the cathodic and anodic processes (80–100 mA h g⁻¹) change insignificantly. The hydrolytic stability, elemental analysis, IR and ESR spectra, DSC–TGA and derivatographic analyses data, the electric conductivity, and the character of the electrochemical activity of the polymers synthesized indicate that the polymers contain the polyvinylene disulfide blocks cross-linked by the polysiloxane chain.

Key words: polydiethylsiloxane, elemental sulfur, sulfurization, electric conductivity, cathodic and anodic processes.

There are few data on reactions of organosilicon compounds with sulfur. It is known^{1,2} that triphenylsilane reacts with sulfur in boiling decalin or without a solvent (200 °C, 11 h) to form triphenylsilanethiol in a yield up to 80%. Under drastic conditions (380 °C), hexabutyl-disilthiane was obtained^{3,4} from tetrabutylsilane and sulfur, presumably through an intermediate tributyl(butylthio)silane. Under comparable conditions, the sulfurization of tetraphenylsilane results in the formation of diphenyl sulfide and "resinification" products.⁴

No reactions of polydiorganylsiloxanes with elemental sulfur were studied, probably because of the traditional concepts on their chemical inertness. At the same time, data on the character of the behavior of siloxanes with respect to such an active and abundant oxidant as sulfur could supplement substantially our knowledge about this important class of chemical compounds, including that about the reactivity and nature of Si–C and Si–O bonds. In addition, products of polysiloxane sulfurization can possess interesting and unexpected properties (electric activity, electric conductivity, and paramagnetism) and, hence, become a basis for the development of new materials.

In this work, we report briefly the results of studying the reactions of polydimethyl- and polydiethylsiloxanes with elemental sulfur.

Taking into account that many organic compounds react vigorously on heating with sulfur to evolve hydrogen sulfide^{4,5} up to the formation of thiocarbonyl groups, we can assume that organic radicals of siloxanes are prone to the same transformations with the formation of cross-linked structures due to polymerization at the C=S bond.

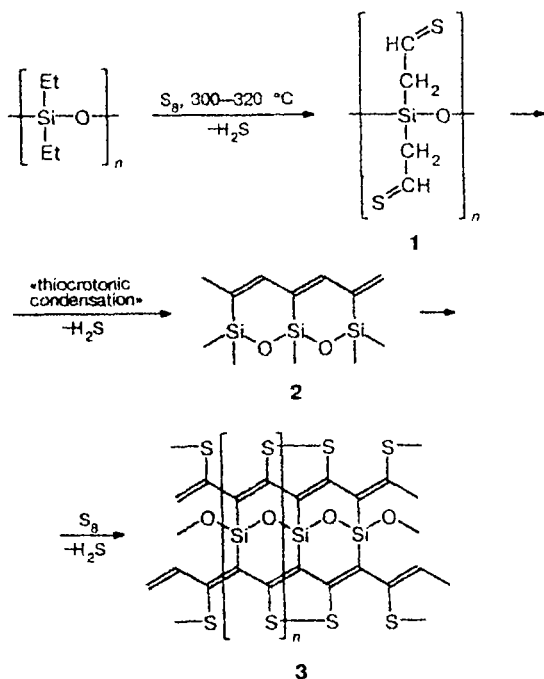
The experiments show that polydimethylsiloxanes with different degrees of polymerization (PMS-3 and PMS-1000) virtually do not react with elemental sulfur at temperatures up to 320 °C (additives of ZnCl₂ have no effect on the result), which confirms the concepts on the high chemical and thermal stability of siloxanes. However, polydiethylsiloxane (PDES) is more reactive with respect to elemental sulfur (Table 1). For example, in the reaction with an excess of sulfur at 300–320 °C, it is transformed by 98% within 2 h into a product insoluble in boiling benzene (the content of S is 18.55%), and hydrogen sulfide is evolved. Additives of iodine and cobalt chloride in amounts of 0.17–0.34% of the weight of the reagents have no noticeable effect on the reaction, according to the sulfur content in the product. The catalytic effect of zinc chloride taken in the same amount has a more certain character: the maximum degree of sulfurization for these conditions is achieved in the presence of 38.50% ZnCl₂ (as compared to 32.44% in the experiment without a catalyst, 7 h). This result corresponds to the

Table 1. Results of the reaction of PDES with elemental sulfur (300–320 °C)^a

Catalyst (wt.%)	<i>t</i> /h	Yield ^b (wt.%)	Found (%)			
			C	H	S	Si
—	2	98			18.55	
—	3	76			23.50	
—	7	113	23.86	4.58	32.44	23.06
I ₂ (0.17)	2	120			25.11	
ZnCl ₂ (0.34)	2	118	23.03	6.10	29.74	24.65
ZnCl ₂ (0.34)	7	110	26.47	4.75	38.50	20.20
I ₂ (0.34)	7	130	20.40	5.00	31.31	22.82
I ₂ (0.34)	2	137	22.63	5.12	31.93	23.78
CoCl ₂ (0.34)	7	118	22.42	4.33	27.80	24.43

^a Loading: 1.02 g of polydiethylsiloxane and 4.80 g of sulfur.^b With respect to the weight of PDES.

insertion of two sulfur atoms into one elemental PDES unit. Since polydimethylsiloxane is inert under these conditions, it is substantiated that in PDES the methyl group, which is more remote from the silicon atom, reacts with sulfur. Then unstable polysiloxane structures with thioformylmethyl groups **1** (Scheme 1) can be intermediate products of PDES sulfuration.

Scheme 1

Black paramagnetic powders ($2 \cdot 10^{18}$ spin g^{-1} , $\Delta H = 0.7$ mT, $g = 2.0043$) with electric conductivity ($\sigma/\text{S cm}^{-1}$) of $4.80 \cdot 10^{-13}$ (in air), $2.90 \cdot 10^{-13}$ (in a vacuum), and $3.20 \cdot 10^{-7}$ (when doped with I₂) are the final products of PDES sulfuration.

The materials obtained are not hydrolyzed by a boiling 25% aqueous solution of NaOH for 5 h, which indicates that they contain no Si—S bonds.⁶ When they are boiled in a 10% aqueous solution of HCl (10 h), a minor amount of hydrogen sulfide is evolved and, correspondingly, the content of sulfur somewhat decreases (from 38.50% to 32.25%), which can be due to the hydrolysis of residual CH=S groups and (or) structures formed during their polymerization ($>\text{CH}-\text{S}-$)_n.

In the IR spectra of the final products, the intensity of absorption bands of the SiCH₂ group (2960, 2940, 2910, 2880, 1450, 1410, 1370, and 1240 cm^{-1})^{7,8} decreases sharply as compared to that of the starting PDES, but a broad absorption band in the 1000–1110 cm^{-1} region characteristic of the Si—O bond^{8,9} remains unchanged.

Sulfurized PDES and the product of its acid hydrolysis possess electrochemical activity. The cyclic voltammograms of these products studied in a three-electrode electrochemical cell exhibit reduction peaks at 2.4 and 2.1 V (Fig. 1). The pronounced peaks were observed only at the first potential scan. The considerable background current in the 2.0–3.0 V region of potentials is related to charging of the double electric layer on the carbon surface and, perhaps, of the polymer. The bilayer (condenser) nature of the background current is indicated by the fact that the currents on the cathodic and anodic plateau of the voltammogram are equal. An increase in the current at potentials lower than 1.8 V is due to the further irreversible reduction of the polymer and components of the electrolyte.

However, the electrochemical activity of sulfurized PDES (both before and after acid hydrolysis) is manifested to a higher extent for the samples obtained in lithium batteries of the disk-type, in which the electrolyte volume is 25-fold lower than that in three-electrode electrochemical cells. The cyclic voltammograms of the polymers have the pronounced reduction peaks at 2.4 and 1.9 V and the oxidation peak at 2.5 V (Fig. 2, a, b). Both polymers exhibit the capability of multiple cyclization in lithium batteries, and the specific capacities of the cathodic and anodic processes decrease insignificantly even after the 12th cycle (Fig. 3).

Thus, sulfurized PDES can be of interest as an active cathode material for lithium batteries.

The chemical, spectral, electrochemical, and physical data obtained agree with the fact that sulfurized

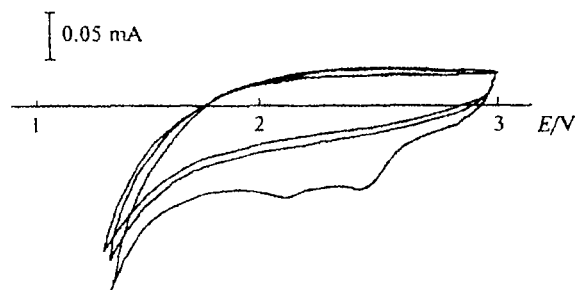


Fig. 1. Cyclic voltammograms of sulfurized PDES (porous Ni electrode, MeOCH₂OMe, 1.0 M CF₃SO₃Li, rel. Li, 1 mV s⁻¹).

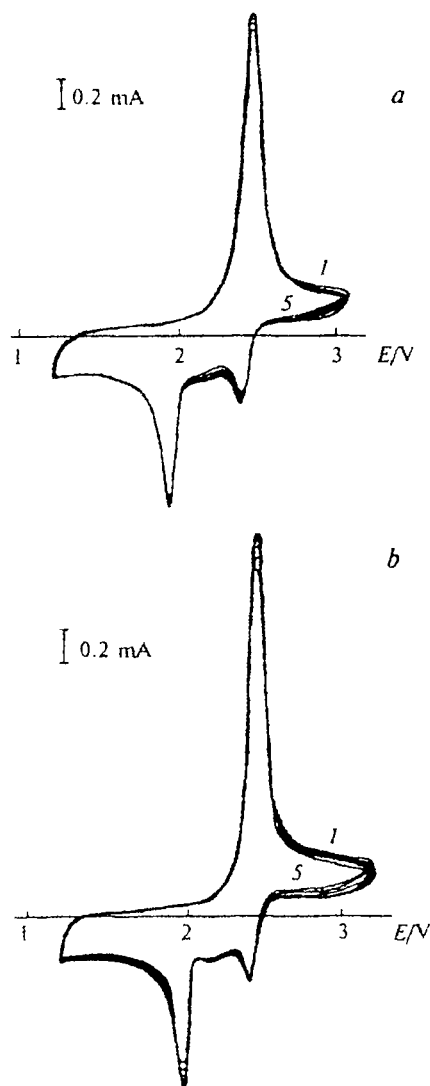


Fig. 2. Cyclic voltammograms of sulfurized PDES (a) and the product of its acid hydrolysis (b) (Al/C electrode, $\text{MeOCH}_2\text{CH}_2\text{OMe}$, $1.0 \text{ M CF}_3\text{SO}_3\text{Li}$, 1 mV s^{-1}). Numbers of cycles are indicated by figures 1–5.

PDES contains polyconjugated structures of type 3 (see Scheme 1), which can be formed due to "thiocrotonic condensation" of intermediate (thioformylmethyl)siloxanes 1 with the further sulfurization of polyacetylene blocks 2 by elemental sulfur.

The presence of S–S bridges in the materials obtained is confirmed by the character of their electrochemical activity. The analysis of the materials by differential scanning calorimetry (DSC) shows (Fig. 4, a) that they contain no elemental sulfur (the absence of endothermic peaks of its melting) and are stable to temperatures of $\sim 390^\circ\text{C}$. At this temperature, an endothermic peak is observed, being transformed into a steep exothermic raise, which most likely corresponds to the cleavage of the S–S bonds in structure 3 with ejection

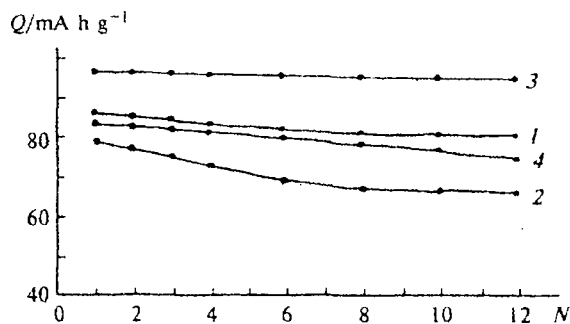


Fig. 3. Dependences of the specific capacity (Q) of sulfurized PDES (1, 2) and the product of its acid hydrolysis (3, 4) on the number of cycles (N) (1, 3, anodic and 2, 4, cathodic processes).

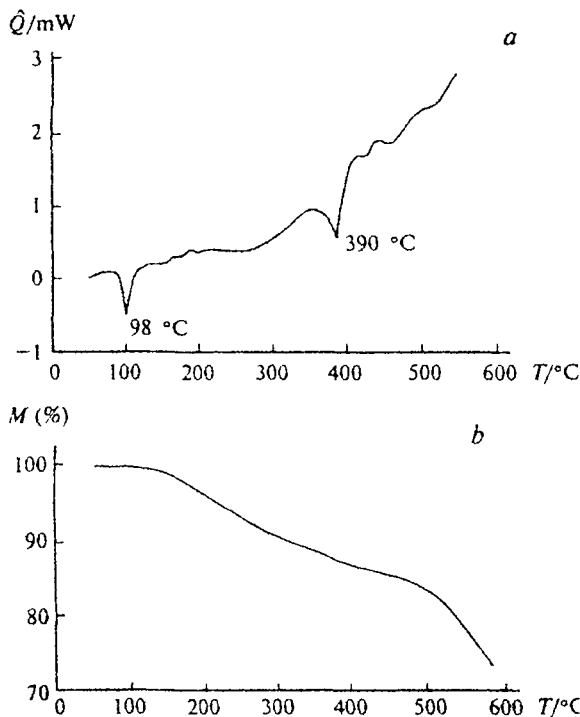


Fig. 4. DSC (a) and TGA (b) curves of sulfurized PDES (S 38.50%). \dot{Q} is heat flow, M is the weight of the sample.

of some sulfur atoms and aromatization ("thiophenization") of the remaining structures. As the thermogravimetric analysis (TGA) shows, at temperatures below $\sim 490^\circ\text{C}$, the sample loses about 16% of its weight (Fig. 4, b, TGA curve), which corresponds to the loss of approximately one sulfur atom in each elementary unit of structure 3. During further heating, the weight loss is accelerated, reaching $\sim 30\%$ near 600°C . This corresponds to the almost complete removal of sulfur atoms and further carbonation of polyacetylene blocks.

The derivatographic analysis (DTA) of sulfurized PDES shows that the thermooxidative decomposition of the sample begins at 250°C with the loss of 7–8% of its initial weight. The noticeable exothermic peak on the

DTA curve with a maximum at 265 °C corresponds to the oxidation of volatile destruction products that formed. This temperature is characteristic of the detachment of lateral substituents of the polyvinylene polymer chain. Probably, the partial detachment and oxidation of the disulfide bridges in structure 3 occur at this stage. The residue is uniformly decomposed with an intense exotherm at temperatures above 330 °C. As the result of the complete decomposition at 550 °C, a white powder (SiO_2), amounting to ~50% of the initial sample weight, remains in the crucible.

The MS study of sulfurized PDES with the maximum sulfur content within the 40–450 °C temperature range confirms the two-stage ejection of sulfur from the polymer (at first it occurs smoothly and then more sharply). The ion diffraction pattern of the thermo-destruction products contains many peaks, among which the two most intense groups are assigned to sulfur S_x ($x = 2-8$), which is confirmed by the mass spectra.

Experimental

IR spectra were recorded on a Specord IR-75 instrument in pellets with KBr.

The specific dark conductivity was measured using a VK 2-16 electrometric amplifier and an E6-13A teraohmmeter. Electrochemical measurements were carried out on a PI-50-1.1 potentiostat using a PDA-1 two-coordinate recorder in the regime of potential cyclization within 1.25–3.00 V with a scan velocity of 1 mV s⁻¹. A three-electrode electrochemical cell and lithium batteries of the disk-type with a lithium counterelectrode and a reference electrode were used. In the first case, a plate of porous nickel (0.5 cm²) was used as the working electrode, and in the second case, an aluminum disk (1 cm²) with the pre-supported composition consisting of the polymer, carbon, and polyethylene oxide in a ratio of 50 : 35 : 15 wt.% was used; a 1 M solution of $\text{CF}_3\text{SO}_3\text{Li}$ in diglyme was used as the electrolyte.

ESR spectra were studied on an SE/X-2547 spectrometer.

DSC analysis was carried out on a DSC-2010 instrument (TA Instrument), and TGA was carried out on a TGA-2050 instrument (TA Instrument). Mass spectra were obtained on a Finnigan GCQ spectrometer with the direct introduction of the polymer into the ionization chamber.

Oxidative thermograms were obtained on a Q derivatograph (MOM, Hungary), using samples with a weight of 50 mg, sensitivity of DTA of 1/5, and the heating velocity of 10 deg min⁻¹.

GLC analysis was carried out on an LKhM-80 gas-liquid chromatograph (a katharometer was used as the detector, column 2500×2 mm, 5% SE-30, Chromaton N-AW, helium).

Polydiethylsiloxane (PDES) is a pentamer. Polydimethylsiloxanes, cyclic trimer (PMS-3) and a mixture of oligomers with the mean molecular weight of ~1000 (PMS-1000), are commercial products.

Sulfurization of polydiethylsiloxane. Polysiloxane PDES (1.02 g, 10 mmol), finely ground elemental sulfur (4.8 g, 150 mmol), and ZnCl_2 (0.02 g) were placed in a glass flask with a thermometer and a reflux condenser attached to a gasometer. The mixture was heated at 300–320 °C for 7 h. Hydrogen sulfide (300 mL) was evolved from the reaction mixture (the positive reaction with $\text{Pb}(\text{OAc})_2$). The solid mass

that formed (4.50 g) was powdered and washed for 10–15 h with boiling benzene in a Soxhlet apparatus to remove a sulfur excess. After drying *in vacuo*, a black lustrous powder with m.p. >350 °C was obtained (1.12 g). Found (%): C, 26.47; H, 4.75; S, 38.50; Si, 20.20. $\text{C}_4\text{H}_6\text{OS}_2\text{Si}$. Calculated (%): C, 29.60; H, 3.73; S, 39.51; Si, 17.30. IR, ν/cm^{-1} : 2960, 2940, 2910, 2880, 1450, 1410, 1370, 1240, 1000–1110 s, 740, 680.

Attempt at sulfurization of polydimethylsiloxane. A. Polysiloxane PMS-3 (0.74 g, 10 mmol), finely ground elemental sulfur (4.8 g, 150 mmol), and ZnCl_2 (0.02 g) were placed in a flask. No hydrogen sulfide is evolved under conditions similar to those used for sulfurization of PDES, and the reaction mixture was completely dissolved in boiling benzene.

B. The treatment of PMS-1000 (0.74 g, 10 mmol) using finely ground elemental sulfur (4.8 g, 150 mmol) and ZnCl_2 (0.02 g) was carried out similarly. Not hydrogen sulfide evolved, and the reaction mixture was completely dissolved in boiling benzene.

Hydrolysis of sulfurization products. A. **Alkaline hydrolysis.** The polymer (1.0 g) obtained from PDES and elemental sulfur was boiled for 5 h with a 25% aqueous solution of NaOH (15 mL). Then the reaction mixture was acidified with diluted hydrochloric acid to pH ~1. The polymer was filtered off, washed with water, and dried *in vacuo* to obtain 0.95 g of the starting polymer (elemental analysis data).

The filtrate was extracted with benzene, and the extract was analyzed by GLC. Not even trace amounts of alkylthiols were observed in the chromatograms.

B. **Acid hydrolysis.** The polymer (1.0 g) obtained from PDES and elemental sulfur was boiled for 10 h in 10% hydrochloric acid (15 mL). Hydrogen sulfide was evolved (the qualitative reaction with lead acetate). The black precipitate was filtered off, washed with water to pH ~6, and dried *in vacuo* to obtain a black powder (0.9 g). Found (%): C, 25.30; H, 4.65; S, 32.25; Si, 28.60. IR, ν/cm^{-1} : 2960, 2940, 2910, 2880, 1450, 1410, 1370, 1240, 1000–1110 s, 740, 680.

References

1. B. Martel, N. Dufaut, and R. Calas, *Bull. Soc. Chim. France*, 1967, 3, 758.
2. M. N. Bochkarev, L. P. Sanina, and N. S. Vyazankin, *Zh. Obshch. Khim.*, 1969, 39, 135 [*Russ. J. Gen. Chem.*, 1969, 39 (Engl. Transl.)].
3. M. Schmidt and H. Schumann, *Z. Chem.*, 1963, 325, 1390.
4. *Reaktsii sery s organicheskimi soedineniyami* [Reactions of Sulfur with Organic Compounds], Ed. M. G. Voronkov, Nauka SO, Novosibirsk, 1979, 368 pp. (in Russian).
5. R. Mayer, *Z. Chem.*, 1976, 16, 260.
6. M. G. Voronkov and N. G. Sviridova, *Usp. Khim.*, 1971, 40, 1761 [*Russ. Chem. Rev.*, 1971, 40 (Engl. Transl.)].
7. L. M. Sverdlov, M. A. Kovner, and E. P. Krainov, *Fizika i tekhnika spektral'nogo analiza. Kolebatel'nye spektry mnogatomnykh molekul* [Physics and Technique of Spectral Analysis. Vibrational Spectra of Polyatomic Molecules], Nauka, Moscow, 1970, 497 (in Russian).
8. A. J. Gordon and R. A. Ford, *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, J. Wiley and Sons, New York–London–Sydney–Toronto, 1972.
9. A. I. Lazarev, A. P. Mirgorodskii, and I. S. Ignat'ev, *Kolebatel'nye spektry slozhnykh oksidov. Silikaty i ikh analogi* [Vibrational Spectra of Complex Oxides. Silicates and Their Analogs], Nauka, Leningrad, 1975, 296 pp. (in Russian).